

# PATENT SPECIFICATION

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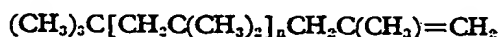
## (54) REINFORCEMENT OF THERMOPLASTIC POLYMERS

(71) We, TBA INDUSTRIAL PRODUCTS LIMITED (formerly Turner Brothers Asbestos Company Limited), a British Company of Asbestos House, Fountain Street, Manchester M2 2EA, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

For various purposes glass fibres are sized. In our Application No. 31550/69 (Serial No. 1278484) glass fibres sized with an olefin having a molecular weight in the range of 200 to 5,000 are described.

We have now found that sized glass fibres as described in our Application No. 31550/69 are particularly valuable for reinforcement of thermoplastic polymers. Also, useful products may be made by impregnation of woven or non-woven fabrics comprising the sized glass fibres with a thermoplastic polymer or by coating one or both surfaces of a woven or non-woven fabric comprising the sized glass fibres with a thermoplastic polymer.

Moulding compositions according to the invention comprise particles of thermoplastic polymer in which are embedded the sized glass fibres. As described in our earlier application the olefin of the size preferably has a terminal olefinic bond or olefinic unsaturation adjacent to one end of the molecule and polybutenes corresponding to the formula

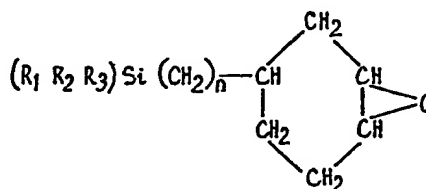


form a preferred class of olefin. Quite generally the olefins may be as described in our earlier application.

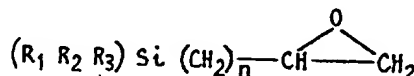
The sizing of the glass fibres may be car-

ried out as described in our earlier application. Thus the olefin may be applied to the fibres as a solution or aqueous dispersion, the concentration of olefin in the solution or dispersion usually being 0.5 to 10% by weight, preferably 2 to 5% by weight, and, in the case of dispersions, a surfactant e.g. the triethanolamine ester of oleic acid may be necessary as a dispersion aid.

Also as described in our earlier application it may be advantageous for the size to include an organo-silicon coupling agent such as a silane or polysiloxane. One useful class of silane corresponds to the general formula:—



in which n is a small positive integer e.g. 1, 2, 3 or 4 and the R groups are readily hydrolysable radicals such as halogen and alkoxy. Another useful class of silane compounds to the formula:—



in which the symbols have the above significance. Still further useful classes of silane are indicated in our earlier application.

The compositions used for sizing the fibres may include yet further components as described in our earlier application e.g. lubricants and anti-foaming agents.

5 The moulding compositions may be made by extrusion compounding the sized glass fibres and polymer and chopping the extruded product into particles. Hot extruded product may be cooled in a water bath and  
10 then cut into particles by a granulator. It is generally convenient for the particles to have a maximum diameter not greater than 5 mm, commonly the particles made by extrusion compounding are substantially rectangular  
15 pellets in which two of the dimensions are about 1 mm whilst the third is about 3 mm. The moulding compositions may also be made by compounding the sized glass fibers and polymer using a heated roller system and  
20 chopping the sheet so obtained into particles, these usually being of irregular shape and of the same order of size as mentioned above. Usually the sized glass fibre content of the moulding composition is at least 10% by  
25 weight, preferably 20 to 35% by weight, but the method just described enables compositions having as much as 80% by weight of size glass fibres to be made conveniently. Compositions having high glass fibre contents  
30 e.g. 50 to 80% by weight can be used as concentrates i.e. they can subsequently be blended with untreated polymer to give moulding compositions of lower glass fibre content e.g. in the range of 20 to 35% by  
35 weight.

The sized glass fibers compounded with the polymer usually are in the form of chopped strands having, for instance, a length  
40 not greater than 25 mm, preferably not greater than 6 mm e.g. 3 to 6 mm. However the fibres may be fed in the form of rovings to an extrusion compounder, in this case the shearing action of the extruder resulting in  
45 chopping of the fibres. Examples of suitable fibre diameters are G, H, J, K and L filament strands i.e. diameters in the range of 9 to 15  $\mu$  m.

The moulding compositions are useful for making moulded articles, e.g. by injection  
50 moulding and can also be used for making extruded particles. Moulded or extruded articles according to the invention are of thermoplastic polymer and are reinforced with the sized glass fibres. Preferably the sized  
55 glass fibres are randomly arranged throughout the articles. By means of the reinforcement improved tensile modulus, flexural modulus and heat distortion temperature can be obtained. Considerable improvement of  
60 the heat distortion temperature can be obtained particularly if the thermoplastic polymer is a semi-crystalline polymer such as a polyamide, polypropylene or polyethylene. In the case of glass-like polymers such as poly-  
65 styrene, styrene-acrylonitrile copolymers, poly-

carbonates, polyphenylene oxides and polymethyl methacrylates the impact strength can be considerably increased by use of the size glass fibres. Other polymers or classes of polymer with which the sized glass fibres are  
70 of value include styrene-acrylonitrile-butadiene terpolymers, polyacetal copolymers, poly(alkylacrylates), poly(alkylmethacrylates) and polyvinyl chloride.

The size of the glass fibres gives them  
75 very desirable processing characteristics when used with thermoplastic polymers and the sized glass fibres also have excellent colour characteristics. In particular, the size greatly  
80 assists compounding of the fibres with the thermoplastic polymers. The olefins used as the sizes tend to have good thermal stability and thus satisfactorily survive high processing  
85 temperatures such as those involved in extrusion compounding and injection moulding. Even if some decomposition does occur at high temperatures it is probably by a process of depolymerization producing volatile,  
90 colourless and non-toxic products which may assist in compounding and moulding operations by acting as release agents. The size may therefore effectively act as a lubricant without adversely affecting the mechanical properties of producing incorporating  
95 the sized glass fibres.

The moulding compositions and moulded and extruded articles may include further materials in addition to the sized glass fibres and the thermoplastic polymers. Thus the inclusion of asbestos fibres can be desirable in  
100 some cases.

The invention is illustrated by the following examples in which the words "Triton", "Propathene", "Lustran", "Cirrasol" and "Maranyl" are all Registered Trade Marks.  
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#### Example 1

The following ingredients were used to form a sizing composition:—

	% by weight	
Polybutene (M.W. 900)	3.0	110
Alkylaryl polyether alcohol (Lenning Chemicals Ltd Triton X100)	0.25	
Silane (Union Carbide, A.1100)	1.0	115
Gelatin	1.0	
Water	94.75	

The silane is 3 - aminopropyl - triethoxy-silane.

The silane was hydrolysed for 30 minutes  
120 in 30% of the water in a suitable container equipped with a variable speed stirrer. Meanwhile the olefin and the alcohol were put in a vessel containing a high speed stirrer and the temperature was raised to 80—85°C. The  
125 stirrer was then started, and sufficient water

at the latter temperature added to invert the initial emulsion to an aqueous dispersion. The gelatin was separately dissolved in water at 60°C and added to the hydrolysed silane.

5 Finally the dispersed olefin was added, and the weight of water adjusted to the given composition. The pH at 20°C was 10.

The composition was used to size 152 tex,

K filament glass strands. The sized glass fibres were then chopped to 6 mm lengths, extrusion compounded with polypropylene powder at 220°C, and injection moulded at 250°C into test pieces complying with British Standard 2782, 301J. The composites and corresponding test pieces not containing the glass fibres gave the following results:

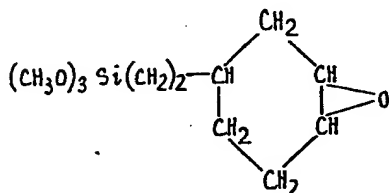
	Polymer type Polymer grade	Polypropylene "Propathene" LY 542M	Polypropylene "Propathene" LY 542M
20	Glass fibre content, % by weight	0	30
	Tensile strength, MN/m <sup>2</sup>	34.0	51.2
	Tensile modulus, GN/m <sup>2</sup>	—	6.2
	Flexural strength, MN/m <sup>2</sup>	—	71.1
25	Flexural modulus, GN/m <sup>2</sup>	1.7 (1700 MPa)	5.3 (5200 MPa)
	Notched Izod, J/m	67	89.1
	Heat distortion temperature at 0.45 MN/m <sup>2</sup> , °C	107	151

#### Example 2

30 The following ingredients were used to form a sizing composition:—

		% by weight
	Polybutene (M.W. 660)	3.0
	Alkylaryl polyether alcohol (Lenning Chemicals Ltd. Triton X100)	0.25
35	Silane (Union Carbide, A.186)	1.0
	Gelatin	1.0
	Water	94.75

The silane corresponds to the formula:—



Example 1. The pH was 6.4 at 20°C.

The composition was used to size 152 tex, K filament glass strands. The sized glass fibres were then chopped to 6 mm lengths, extrusion compounded with polystyrene beads at 175—230°C, and injection moulded at 240°C into test pieces complying with British Standard 2782, 301J. The composites and corresponding test pieces not containing the glass fibres gave the following results:—

40 The composition was prepared as in

	Polymer type Polymer grade	Polystyrene "Carinex" GP	Polystyrene "Carinex" GP
	Glass fibre content, % by weight	0	25
55	Tensile strength, MN/m <sup>2</sup>	41.0	70.7
	Tensile modulus, GN/m <sup>2</sup>	3.5	7.7
	Flexural strength, MN/m <sup>2</sup>	68.4	93.9
	Flexural modulus, GN/m <sup>2</sup>	3.5	6.8
	Notched Izod, J/m	21	64.1
60	Heat distorting temperature, at 0.45 MN/m <sup>2</sup> , °C	85	96

#### Example 3

65 Sized glass fibres identical to those of Example 2 were extrusion compounded with styrene-acrylonitrile copolymer (SAN) at 175—230°C, and injection moulded at 240°C

into test pieces complying with British Standard 2782, 301J. The composites and corresponding test pieces not containing the glass fibres gave the following results:—

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	Polymer type Polymer grade	SAN "Lustran" 28	SAN "Lustran" 28
	Glass fibre content, % by weight	0	25
5	Tensile strength, MN/m <sup>2</sup>	65.0	94.0
	Tensile modulus, GN/m <sup>2</sup>	3.0	9.5
	Flexural strength, MN/m <sup>2</sup>	95	147.0
	Flexural modulus, GN/m <sup>2</sup>	3.2	8.6
	Notched Izod, J/m	21.3	42.7
10	Heat distortion temperature, at 0.45 MN/m <sup>2</sup> , °C	85	101

#### Example 4

The following ingredients were used to form a sizing composition:—

	% by weight
Polybutene (M.W. 1300)	3.0
Alkylaryl polyether alcohol (Lenning Chemicals Ltd. Triton X100)	0.25
Silane	1.0
Cationic lubricant (I.C.I. Ltd. Cirrasol FG)	0.10
25 Gelatin	1.0
Water	94.65

The silane was the same as that used in Example 1. The cationic lubricant specified is believed to be a condensation product of a pentamine with a mixture of long chain fatty acids such as stearic and palmitic acids. The silane was hydrolysed for 30 minutes in 30% of the water in a suitable container

equipped with a variable speed stirrer. Meanwhile the olefin and the alcohol were put in a vessel containing a high speed stirrer and the temperature was raised to 85—90°C. The stirrer was then started, and sufficient water at the latter temperature was added to invert the initial emulsion to an aqueous dispersion. The gelatin and the lubricant were separated dissolved in water at 60°C and added to the hydrolysed silane. Finally the dispersed olefin was added, and the weight of water adjusted to the given composition. The pH at 20°C was 10.5.

The composition was used to size 152 tex, K filament glass strands. The sized glass fibres were then chopped to 6 mm lengths, extrusion compounded with polycaprolactam (nylon 6) pellets at 240°C and injection moulded at 270°C into test pieces complying with British Standard 2782, 301J. The composites and corresponding test pieces not containing the glass fibres gave the following results:—

	Polymer type Polymer grade	Nylon 6 "Maranyl" F114	Nylon 6 "Maranyl" F114
	Glass fibre content, % by weight	0	30
60	Tensile strength, MN/m <sup>2</sup>	81.0	163.5
	Tensile modulus, GN/m <sup>2</sup>	—	10.3
65	Flexural strength, MN/m <sup>2</sup>	97.5	257.2
	Flexural modulus, GN/m <sup>2</sup>	2.1	8.3
	Impact Izod, J/m	53.4	101.4
70	Heat distortion temperature, at 0.45 MN/m <sup>2</sup> , °C	150	212

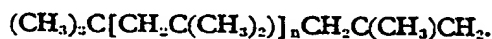
#### WHAT WE CLAIM IS:—

1. A moulding composition comprising particles of thermoplastic polymer in which are embedded glass fibres sized with an olefin having a molecular weight in the range of 200 to 5,000.

2. A moulding composition according to claim 1 in which the olefin has a terminal olefinic bond.

3. A moulding composition according to

claim 2 in which the olefin is a polybutene of general formula



4. A moulding composition according to any preceding claim in which the size on the glass fibres includes a silane or a polysiloxane as well as the olefin.

5. A moulding composition according to

any preceding claim in which the maximum dimension of the particles is not greater than 5 mm.

5 6. A moulding composition according to any preceding claim in which the thermoplastic polymer is a polyamide, a polyethylene or a polypropylene.

10 7. A moulding composition according to any of claims 1 to 5 in which the thermoplastic polymer is a polystyrene or a styrene-acrylonitrile copolymer.

15 8. A moulding composition according to any of claims 1 to 5 in which the thermoplastic polymer is a polycarbonate or a polyphenylene oxide.

9. A moulding composition according to any preceding claim comprising up to 80% by weight of the sized glass fibres.

20 10. A moulding composition according to claim 9 comprising 20 to 35% by weight of the sized glass fibres.

11. A moulding composition according to any preceding claim in which asbestos fibres are also embedded in the particles.

25 12. A moulding composition according to claim 1 substantially as hereinbefore described with reference to any of the Examples.

30 13. A moulded or extruded article made from a moulding composition according to any of claims 1 to 12.

14. A moulded or extruded article of thermoplastic polymer reinforced with glass fibres sized as specified in any of claims 1 to 4.

35 15. An article according to claim 14 in

which the thermoplastic polymer is as specified in claim 6.

16. An article according to claim 14 in which the thermoplastic polymer is as specified in claim 7.

17. An article according to any of claims 14 to 16 in which the glass fibres are randomly arranged throughout the article.

18. An article according to any of claims 14 to 17 in which the thermoplastic polymer is reinforced with asbestos fibres as well as with the sized glass fibres.

19. A woven or non-woven fabric comprising glass fibres sized as specified in any of claims 1 to 4 impregnated with a thermoplastic polymer.

20. A fabric according to claim 19 in which the thermoplastic polymer is as specified in claim 6.

21. A fabric according to claim 19 in which the thermoplastic polymer is as specified in claim 7.

22. A woven or non-woven fabric of glass fibres sized as specified in any of claims 1 to 4 and having a coating, on at least one surface, of a thermoplastic polymer.

23. A fabric according to claim 22 in which the thermoplastic polymer is as specified in claim 6.

24. A fabric according to claim 22 in which the thermoplastic polymer is as specified in claim 7.

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